UNIVERSITI PUTRA MALAYSIA

PHOTOPYROELECTRIC TECHNIQUE IN THERMAL DIFFUSIVITY DETERMINATION AND SPECTROSCOPIC RESPONSE OF SOLID SAMPLES

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By

LIAW HOCK SANG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

August 2003

SPECIALLY DEDICATED TO MY BELOVED FAMILY MEMBERS AND LAU SIEH HIE

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

PHOTOPYROELECTRIC TECHNIQUE IN THERMAL DIFFUSIVITY DETERMINATION AND SPECTROSCOPIC RESPONSE OF SOLID SAMPLES

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August 2003

Chairman : Azmi Zakaria, Ph.D.

Faculty : Science and Environmental Studies

Conventional photopyroelectric (PPE) measurement of thermal diffusivity of optically opaque sample was done in case of thermally thick sample, but it underwent a great attenuation of signal. In this study, the generalisation of Mandelis and Zver special cases of thermally thin-thick sample has been derived and was used to determine the thermal diffusivity. The method was experimentally tested for aluminium samples of different thickness and copper sample, and the values obtained were close to the literature values.

The Bennett and Patty theory in the generation of photoacoustic signal has been successfully adopted in the generation of PPE signal. An equation of complex PPE signal was derived. A normalisation procedure was used to eliminate a number of unknown parameters in PPE cell. The method was experimentally tested for aluminium, copper, and nickel samples, and the values obtained were close to the literature values.

Previous data acquisition program written in QBASIC has been modified to further increase the spectrometer reliability and performance. The method of getting both the optical and the thermal transmission spectra of solid samples has demonstrated by using an intact green leaf and by poly (methyl methacrylate) doped with methyl red polymer. These spectra showed a strong inversion between each other, and were obtainable on the exactly same sample and detector by simply varying the light chopping frequency.

The thermal transmission spectrum was used to determine the band-gap energy of the ZnO substituted with different CoO mol percentage. The powdered samples were prepared in a thickness that the spectrum is obtainable. Even though the prepared sample was deposited on a 50μm-thick stainless steel substrate, which was totally opaque, the unsaturated thermal transmission spectra have been obtained. This suggests that thin film deposited on opaque substrate can be studied with current PPE system. The band-gap energy of ZnO is 3.16eV and that of CoO-substituted ZnO decreases as the CoO mol% increases.

The monochromator was replaced by a motorised monochromator to further increase the performance of PPE spectrometer system. A PCI I/O card was used to add two more COM ports. Utility program, which was written in LabVIEW programming language served as data acquisition program for the new monochromator, has been successfully modified to integrate with lock-in amplifier. This system was applied to Neodymium oxide sample in UV-VIS regions. In this case, less sample preparation was required and the peaks at spectrum were in good agreement with literatures.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains.

TEKNIK FOTOPIROELEKTRIK DALAM PENENTUAN KERESAPAN TERMA DAN RESPONS SPEKTROSKOPI BAGI SAMPEL-SAMPEL PEPEJAL

Oleh

LIAW HOCK SANG

Ogos 2003

Pengerusi : Azmi Zakaria, Ph.D.

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Pengukuran fotopiroelektrik (PPE) lazim bagi keresapan terma bagi sampel legap telah dibuat dalam kes sampel yang tebal secara terma, tetapi ia mengalami pengecilan isyarat yang besar. Dalam kajian ini, kesimpulan umum kes-kes khas Mandelis dan Zver bagi sampel nipis-tebal secara terma telah diterbitkan dan telah digunakan untuk menentukan keresapan terma. Kaedah ini telah diuji secara experimen pada sampel aluminium yang berlainan ketebalan dan sampel tembaga. Nilai-nilai yang diperolehi adalah menghampiri nilai-nilai literatur.

Teori Bennett dan Patty dalam penjanaan isyarat fotoakustik telah berjaya dicerapkan dalam penjanaan isyarat PPE. Satu persamaan kompleks isyarat PPE telah diterbitkan. Prosedur normalisasi telah digunakan untuk menghapuskan sebilangan parameter yang tidak diketahui dalam sel PPE. Kaedah ini telah diuji secara eksperimen bagi sampel aluminium, tembaga, dan nikel. Nilai-nilai yang diperolehi adalah hampir dengan nilai-nilai literatur.

Program pemerolehan data sebelumnya yang ditulis dalam QBASIC pada spektrometer PPE telah diubahsuai untuk meningkatkan kebolehpercayaan dan prestasinya. Kaedah untuk mendapatkan kedua-dua spektrum transmisi optik dan terma bagi sampel pepejal telah didemonstrasi dengan menggunakan daun hijau dan polimetilmetakrilat yang didopkan dengan metil merah. Spektrum-spektrum ini menunjukkan songsangan yang kuat di antara satu sama lain dan boleh diperolehi pada sampel dan pengesan yang sama dengan hanya mengubahkan frekuensi pencantas cahaya.

Spektrum-spektrum transmisi terma telah digunakan untuk menentukan tenaga jurang-jalur bagi ZnO yang digantikan dengan CoO yang berlainan peratus molnya. Sampel serbuk itu telah disediakan dengan ketebalan yang membolehkan spektrum itu diperolehi. Walaupun sampel itu didiposisi di atas substrak keluli tahan karat yang berketebalan $50\mu m$ dan betul-betul legap, spektrum transmisi terma tak-tepu telah diperolehi. Ini mencadangkan bahawa filem yang didiposisi di atas substrak legap boleh dikaji dengan sistem PPE ini. Tenaga jurang-jalur bagi ZnO ialah 3.16eV dan ZnO yang digantikan dengan CoO, tenaga ini menurun dengan peningkatan mol% CoO.

Monokromator telah digantikan dengan suatu monokromator yang bermotor untuk meningkatkan prestasi sistem spektrometer PPE. Satu kad PCI I/O telah digunakan untuk menambahkan dua lagi port COM. Progam utiliti yang ditulis dalam bahasa pengaturcaraan LabVIEW yang diguna sebagai program pemerolehan data bagi monokromator baru itu telah berjaya diubahsuaikan untuk berintegrasi dengan amplifier lock-in. Sistem ini telah diaplikasikan bagi sampel Neodimium oksida dalam rantau UV-VIS. Dalam kes ini, penyediaan sampel hampir tidak diperlukan dan puncak-puncak spektrum yang terhasil adalah berpadanan dengan literatur.

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I certify that an Examination Committee met on 4th August 2003 to conduct the final examination of Liaw Hock Sang on his Master of Science thesis entitled "Photopyroelectric Technique in Thermal Diffusivity Determination and Spectroscopic Response of Solid Samples" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

LiawHockSang

LIAW HOCK SANG

Date : 26 SEP 2003

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LIST OF ABBREVIATIONS

BPPE	Back-detection PPE
FPPE	Front-detection PPE
IPPE	Inverse PPE
LabVIEW	Laboratory Virtual Instrument Engineering Workbench
MOR	Modulated optical reflectance
MR	Methyl red
NC-BPPE	Non-Contact-Back PPE
NC-FPPE	Non-Contact-Front PPE
OBD	Optical beam deflection
PA	Photoacoustic
PAS	Photoacoustic spectroscopy
PDS	Photothermal deflection spectroscopy
PMMA	Poly (methyl methacrylate)
PE	Pyroelectric
PPE	Photopyroelectric
PT	Photothermal
PTD	Photothermal displacement
PTR	Photothermal radiometry
PVDF	Polyvinylidene diflouride
PZ	Piezoelectric
RPPE	Reflective PPE
SPPE	Standard PPE
VIs	Virtual instruments

LIST OF SYMBOLS

α	Thermal diffusivity
b	Ratio of thermal effusivities
β	Optical absorption coefficient
c	Specific heat
e	Thermal effusivity
E_g	Energy gap
ε	Dielectric constant
ε_o	Vacuum permittivity
f	Modulation frequency
hv	Quantized photon energy
i	$\sqrt{-1}$
I_o	Optical intensity
k	Thermal conductivity
l_β	Optical absorption length
m	Slope or gradient
L	Thickness
λ	Wavelength
η	Light-to-heat conversion efficiency
p	Pyroelectric coefficient
ρ	Density
Q_o	Heat source intensity
R_n	Thermal wave reflection coefficient
$R(\lambda)$	Optical reflectivity at wavelength λ
T_n	Thermal wave transmission coefficient
μ.	Thermal diffusion length
ω	Angular modulation frequency.

CHAPTER 1

INTRODUCTION

1.1 Photothermal Spectroscopy

Spectroscopy is concerned with the study of the interaction of light energy with matter covering many techniques and disciplines. Conventional optical spectroscopy is the earliest form of spectroscopy in studying the optical energy with respect to wavelength in the form of photons that are transmitted through, scattered or reflected from the material under investigation. The respective wavelength of the optical energy is ranging from less than 1Å in the X-ray region to 100μm in the far-infrared region. A plot of the data recorded by detecting these photons after their interaction with the material is called a spectrum (Rosencwaig, 1978; 1980).

In spites of its long history, optical spectroscopy is still the most used and active spectroscopic field, partly, because it forms a nondestructive investigation materials. However, the conventional transmission and reflection type of optical spectroscopy is not readily to work with materials in a wide variety of physical forms, especially those materials with (Rosencwaig, 1978; 1980; Miller, 1987):

i. very low optical density,

ii. very high optical density,

iii. light scattering, and

iv. specularly reflecting materials.

These materials include transparent gas mixtures containing small quantities of absorbing species or pollutant, window materials, powders, amorphous solids, intact biological samples, and thin films.

Over the years, several techniques have been developed to allow optical investigation of such materials. Diffuse reflectance, attenuated total reflection (or internal reflection spectroscopy), and Raman scattering were among the techniques invented. All these techniques have been found to be very useful for a small category of materials over a small range of wavelength.

Photopyroelectric (PPE) spectroscopy is one of the several photothermal (PT) spectroscopic techniques that is suitable to study those materials. In conventional techniques, the interaction of these photons with the material under study is investigated through subsequent detection and analysis of the photons. In PT techniques, even though the incident energy is in form of photons, the subsequent detection and analysis is a direct measure of the energy absorbed by the material due to its interaction with the photon beam. Energy absorbed is partly converted into heat as result of non-radiative de-excitation. Since the sample heating is a direct consequence of optical absorption, the PT signal is directly dependent on light absorption. Reflection and scattering loses do not produce PT signal and do not cause serious problems in photothermal spectroscopy (Bialkowski, 1996).

PT science covers a wide range of techniques and phenomena to study optical and thermal characteristic of a sample based upon a subsequence effect of the conversion of absorbed optical energy into heat. The basis of the PT process is a photo-induced change in their thermal state of the sample. The state of the sample can be in form of solid, liquid, or gas. In all PT systems, a modulated or pulsed excitation source is used to generate periodic or transient heating, respectively, in the sample. In a series of non-radiative de-excitation, the absorbed optical energy is converted into thermal energy. This thermal energy causes a number of physical changes in and around the sample. Figure 1.1 is a schematic illustration of the phenomena resulting from the exposure of a sample surface to periodically modulated light source. These effects form the basis of several detection schemes, which are divided into three detection groups: acoustic, optical and thermal detection.

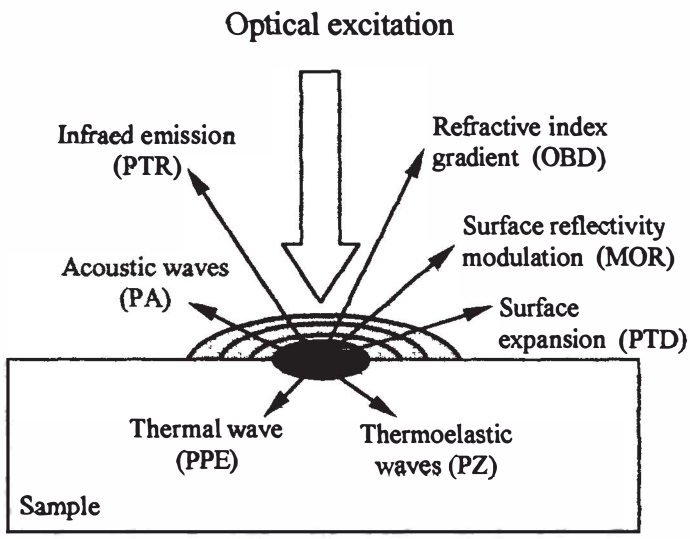

Figure 1.1: PT phenomena caused by illumination of a surface by modulated beam of light with corresponding detection technique in parenthesis (Almond and Patel, 1996).

1.2 Photopyroelectric Detection

Pyroelectricity is the property of certain material to produce a state of electrical polarization due to the change of temperature. This spontaneous or frozen